

# INDUSTRIAL EXPERIENCE

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## UNFRITTED OPAQUE GLAZE FOR CERAMIC SANITARWARE

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The possibility of fabricating unfritted opaque glaze roasted at a high temperature (1200°C) for ceramic sanitarware is considered. The glaze contains finely disperse zircon and possesses high whiteness.

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Power can be saved in the production of ceramic sanitarware by using unfritted opaque glaze. Another important direction consists in improving the quality of the glazed surface.

The present work has been aimed at creating a composition for unfritted opaque glaze for high-temperature roasting (1280°C) that would possess high whiteness and at finding optimum conditions for opacifying the glaze with zircon  $\text{ZrSiO}_4$ .

Glasses and glazes can be opacified as a result of drop segregation or the presence of crystals in the glass; the degree of opacification is higher the greater the difference in the refractive indices of the phases present in the glass.

Since high-temperature glazes are represented by refractory glass, it is difficult to obtain opacified coatings from them because drop segregation is unlikely in such glasses. This group includes crystallized coatings opacified by one crystalline phase with quite coarse grains (larger than 1  $\mu\text{m}$ ) that can be positioned nonuniformly, leaving considerable regions of the glass quite pure.

Such a coating is opacified due to the distribution of solid particles in it, which possess a different refractive index from the glass phase and scatter the incident light due to reflection, refraction, and diffraction. The light rays incident on the surface of the coating are partially reflected from it and partially pass into it. In addition, the light rays undergo repeated refraction and reflection in all directions from the solid particles of the opacifier; this process is called light scattering.

In accordance with the Rayleigh law the optimum size of the crystal grains of the opacifier that provides maximum dulling is 0.2–1.0  $\mu\text{m}$ . The intensity of light scattering due to refraction from highly disperse crystalline particles is directly proportional to the difference in the refractive indices of the particles and the glass phase of the coating. Zircon

with a refractive index of 1.85, which exceeds that of the glass phase (1.52), is most widely used for opacifying ceramic glazes. The light scattering due to refraction increases with the number of crystalline particles, i.e., with the degree of their dispersity.

Opacified fritted glaze is obtained using commercial zircon concentrate that contains 97% particles less than 63  $\mu\text{m}$  in size and 3% particles larger than 63  $\mu\text{m}$ .

Based on the results on many studies we can state that this material is not effective for opacifying unfritted glaze and should therefore be milled additionally. Zircon is milled by the wet method in a ball mill. The grain size after 100-h preliminary milling is 20–30  $\mu\text{m}$ .

With increase in the maximum roasting temperature the viscosity of the molten glaze is improved. The cooling rate in the crystallization range ( $T_L - T_S$ ) should not hamper full recrystallization of the opacifier. The recrystallization is accompanied by dispersion of the grains of the opacifier with respect to the initial grain size.

The grains of recrystallized zircon in the crystallized coating are comparatively large, and therefore the whiteness of the coating is not good enough even when its content is high.

The solubility of zircon in green glazes (even at a high temperature (1280°C)) is less than in frits molten at 1400°C. Therefore, the predominant portion of the zircon in unfritted coatings remains in a suspended state.

Finely disperse zircon of grade Zirkobit MO bears 50% grains 1.45  $\mu\text{m}$  in size and 50% grains over 5  $\mu\text{m}$  in size; Zirkobit MOS contains 50% grains 1.1  $\mu\text{m}$  in size and 50% grains with a maximum size of 5  $\mu\text{m}$ . The chemical composition (in mass fractions) is 63.92–64.32%  $\text{ZrO}_2$ , 31.88–32.02%  $\text{SiO}_2$ , 0.07–0.08%  $\text{Fe}_2\text{O}_3$ , 0.11–0.12%  $\text{TiO}_2$ , and 1.33–1.87%  $\text{Al}_2\text{O}_3$ .

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An analysis of studies devoted to the mechanism of opacification of high-temperature glazes performed by the research laboratory of the Samarskii Stroifarfor JSC allowed its workers to develop an unfritted opacified glaze with enhanced whiteness. The chemical composition of the glaze (in mass fractions) is 51.38%  $\text{SiO}_2$ , 9.32%  $\text{Al}_2\text{O}_3$ , 0.15%  $\text{Fe}_2\text{O}_3$ , 7.41%  $\text{CaO}$ , 1.85%  $\text{MgO}$ , 2.96%  $\text{ZnO}$ , 4.63%  $\text{BaO}$ , 9.05%  $\text{ZrO}_2$ , 1.04%  $\text{Na}_2\text{O}$ , 3.73%  $\text{K}_2\text{O}$ , 8.17 calcined losses; the TCLE of the mix is  $(6.58 - 7.06) \times 10^{-6} \text{ K}^{-1}$ , and the TCLE of the glaze is  $(6.52 - 6.98) \times 10^{-6} \text{ K}^{-1}$ .

The raw materials for the mix are feldspar of the Chupinskoe deposit, quartz sand, zinc oxide, barium carbonate, chalk, talc, kaolin, refractory clay, and Zirkobit MO. The green glaze is prepared by joint milling of all the components to a residue of 0.15 – 0.20% on screen No. 0063.

The density of the glaze suspension to be deposited on the articles by immersion is  $1640 \text{ kg/m}^3$  and that for pulverization is  $1700 - 1730 \text{ kg/m}^3$ .

In order to increase the milling efficiency we used a deflocculating agent, namely, sodium hexametaphosphate. In

order to control the properties of the glaze suspensions we used an organic thinner (Riotan).

The introduction of finely milled zircon into the composition of unfritted glaze yields opacified white glaze with a whiteness exceeding that of the articles. The degree of opacification of a glaze containing finely disperse zircon is higher the finer the particles of the opacifier, other conditions being equal.

When the green glaze melts, zircon does not decompose noticeably or interact with the other components of the glass. However, noncrystallization processes can occur in the glaze due to dissolution of fine reaction-capable zircon particles and subsequent crystallization of zircon crystals from the melt; the latter are finer, have well-shaped faces, and are uniformly distributed in the volume of the glass. This explains the high efficiency of the opacification of the unfritted glaze by finely disperse zircon and the elevated whiteness of the surface of the ceramic sanitarware.